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ATTENUATION LENGTHS OF PHOTOELECTRONS IN HYDROCARBON FILMS

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# Attenuation Lengths of Photoelectrons in Hydrocarbon Films

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**Abstract:** The attenuation length,  $\lambda$ , of photoelectrons with energies in the range 900–1400 eV in hydrocarbon films was measured using self-assembled monolayers of alkanethiols,  $\text{HSC}_n\text{H}_{2n+1}$ , on gold. The intensity of the photoelectron peaks from the gold substrate decreased exponentially with the chain length, with attenuation lengths of 42 Å at 1402 eV, 34 Å at 1151 eV, and 28 Å at 940 eV. Over the narrow energy range studied,  $\lambda$  was directly proportional to the kinetic energy of the photoelectrons.

Quantitative analysis of data obtained by X-ray photoelectron spectroscopy (XPS) requires a knowledge of the escape depths of electrons from the surface of a sample.<sup>1</sup> In order to derive the composition of a homogeneous material from the intensities of the photoelectrons originating from different elements, one needs to know not only the relative atomic cross-sections, but also the variation of the attenuation length,  $\lambda$ , with the energy of the photoelectrons.<sup>2</sup> The ability to derive an elemental depth profile of a layered material from the variation in the photoelectron intensity with the angle of emission requires a knowledge of the absolute value of  $\lambda$ .<sup>3</sup>

The recent growth of interest in thin (< 10 nm) organic films<sup>4</sup> has generated an immediate need for accurate, reliable values of  $\lambda$  in organic materials in general, and in thin, densely packed hydrocarbon films in particular. In this paper we have determined the attenuation length of electrons with energies in the range 940–1400 eV in self-assembled monolayers of *n*-alkanethiols ( $\text{HSC}_n\text{H}_{2n+1}$ ;  $n = 6, 8, 9, 11, 12, 14, 16, 17, 18, 20, 22$ ) adsorbed on gold.

There are two main approaches to obtaining the attenuation length in the surface of a solid. In one technique,<sup>5</sup> the absolute intensity of an XPS peak from the sample is compared with the signal from a standard, usually gold. Accurate determinations of  $\lambda$  require not only that the atomic cross-sections in both the sample and the standard, and of  $\lambda$  in the standard be known, but also that the two surfaces be free of contamination and that both have the same surface morphology – requirements that are often hard to meet. The alternative approach, which we adopt here, is to measure the attenuation of the photoelectrons from a substrate with variation in the thickness of an overlayer film.<sup>6–9</sup> The principal requirement for this technique to work well is that the overlayer should be homogeneous and of a known thickness: no knowledge is required of atomic cross-sections or of the attenuation length in a standard. Self-assembled monolayer films are ideal for these studies since they form uniform films with well-defined structure and

thickness.<sup>10,11</sup>

The literature values<sup>12</sup> for escape depths in organic materials vary widely: at 1000 eV, values from 15 Å to over 100 Å have been reported.<sup>6,7</sup> Swalen et al<sup>9</sup> resolved some of the confusion by studying the attenuation of photoelectrons from gold, silver and indium substrates by multilayers of cadmium arachidate ( $[\text{C}_{19}\text{H}_{39}\text{CO}_2^-]_2\text{Cd}^{2+}$ ) applied by the Langmuir-Blodgett technique.<sup>13</sup> They obtained values of  $\lambda = 36$  Å at 1042 and 1117 eV, and 41 Å at 1402 eV. These values of  $\lambda$  are not the values for pure hydrocarbon, however, since a cadmium carboxylate layer, together with an undetermined amount of tightly associated water, was incorporated into the film with each monolayer of hydrocarbon. In addition, the calculations were complicated by necessary corrections for exposed bare patches on the substrate. Electrochemical studies on monolayers of thiols on gold<sup>14</sup> have shown a negligible density of pin-holes and thus no such corrections are required here. More recently, Tougaard and Sigmund<sup>15</sup> have shown theoretically that the observed value of  $\lambda$  may vary considerably with the thickness of the overlayer due to elastic scattering of the photoelectrons. Studies of monolayers thus provide a useful comparison with the data obtained from multilayers of cadmium arachidate.<sup>9</sup>

Here we present data for the attenuation of Au(4f<sub>7/2</sub>), Au(4d<sub>5/2</sub>) and Au(4p<sub>3/2</sub>) photoelectrons (with kinetic energies of 1402, 1151 and 940 eV, respectively) from the gold substrate by a hydrocarbon overlayer (Figure 1), the thickness of which was varied from 7 to 24 Å. We also compare the intensities of the C(1s) photoelectrons with those predicted from a simple model.

## Experimental Section

The gold substrates were prepared by evaporation of ~1000 Å of gold onto silicon (111) wafers that had been coated with ~50 Å of chromium to promote adhesion. Previous SEM and TEM studies have indicated that the surface morphology consists of low rolling

hills, a few hundred angstroms across, and broad plateaus of (111) surface.<sup>16</sup> The gold-coated wafers were cut into slides (1 cm X 3 cm) and immersed in ~1 mM solutions of the alkanethiols in oxygen-free ethanol, overnight at room temperature.<sup>10</sup>

External reflection infrared spectroscopy indicates that, for  $n > 9$ , these monolayers are densely packed with the monolayer axis tilted approximately  $30^\circ$  from the normal to the surface.<sup>14</sup> For shorter chains, the monolayers may be disordered or oriented slightly differently,<sup>17</sup> but these differences in structure are not necessarily accompanied by changes in the number of molecules adsorbed per unit area.

XPS spectra were collected on a Surface Science Instruments spectrometer (Model SSX-100) with a monochromatized Al  $K\alpha$  source, concentric hemispherical analyzer operating in fixed analyzer transmission mode, and a multichannel detector. The spectra were acquired with a 100 eV pass energy, and 600- $\mu\text{m}$  spot.<sup>18</sup> The samples were analyzed in a random order. Four peaks were collected on each sample: Au(4f<sub>7/2</sub>) (15 eV window, 1 scan (approximately 1 minute)), Au(4d<sub>5/2</sub>) (25 eV, 2 scans), Au(4p<sub>3/2</sub>) (25 eV, 4 scans) and C(1s) (15 eV, 4 scans). Radiation damage was insignificant over the acquisition times used. The dead time of the detector was always less than 10%. The same background limits and peak shapes were used for each sample, with a Shirley background subtraction.<sup>19</sup>

## Results

**Attenuation of photoelectron peaks from the gold substrate.** To analyze the intensities of the gold peaks we assume that they follow eq 1

$$Au_n = Au_0 e^{-n d / \lambda \sin \theta} \quad (1)$$

where  $Au_n$  = the intensity of the gold photoelectrons attenuated by an  $n$ -carbon monolayer

$Au_0$  = the intensity from clean gold<sup>20</sup>

$b$  = constant correction term arising from the gold-sulfur interface

$n$  = number of carbon atoms in each chain

$d$  = thickness of the monolayer per methylene ( $CH_2$ ) unit

$\lambda$  = attenuation length

$\theta$  = the angle between the surface parallel and the analyzer axis (take-off angle).

Taking logarithms, eq 1 yields

$$\ln(Au_n) = -nd/\lambda \sin\theta + \text{constant} \quad (2)$$

A graph of  $\ln(Au_n)$  against  $n$  should yield a straight line with slope of  $d/\lambda \sin\theta$ , from which  $\lambda$  can be calculated. Any variations in  $d$  or  $\lambda$  with  $n$  will be evident as curvature in the data.

Figure 2 plots the core-level gold intensities against  $n$ . Linear fits to the data are shown. To convert the slopes to attenuation lengths we use a value of  $d = 1.1 \text{ \AA} = 1.27 \cos 30^\circ$ , where  $1.27 \text{ \AA}$  is the incremental chain length per methylene group (inferred from X-ray diffraction studies of solid paraffins<sup>21</sup>), and  $30^\circ$  is the mean tilt of the chain from the surface normal (calculated from infrared spectra<sup>14</sup>). The chain axis does not match the take-off angle of  $35^\circ$ ,<sup>22</sup> so we do not expect any artifacts due to channelling of the photoelectrons along the chain direction.<sup>23</sup> Table I gives the slopes, and the derived values of  $\lambda$ .

In addition to the random error (given in Table I), there are several sources of systematic error in our determination of  $\lambda$ . First, the limit of error in the determination of the tilt of the hydrocarbon chains by IR is  $\pm 5^\circ$ , resulting in an uncertainty of  $\pm 5\%$  in the calculated value of  $\lambda$ .

Second, the analyzer lens has a finite acceptance angle ( $30^\circ$ ). Since photoelectron emission from the surface decreases with decreasing take-off angle, higher take-off angles

are weighted more heavily in the acquired signal. For example, if the photoelectrons are emitted with a cosine distribution,<sup>24</sup> and we assume that the transmission function is constant over the analyzer lens, then the mean take-off angle of the detected photoelectrons is 36.5°, compared with 35° on the lens axis -- an increase of 4% in  $\sin \theta$ . An exact calculation of the effect on the measured value of  $\lambda$  is more complicated, but will still result in an overestimation of  $\lambda$ .<sup>25</sup>

Third, roughness of the surface causes a small underestimation of  $\lambda$  at high take-off angles, and a large overestimation at grazing angles.<sup>26</sup> The deviation depends both on the length scale and the type of roughness. Although our evaporated gold films are smooth compared to most surfaces, roughness probably still causes a small overestimation in the value of  $\lambda$ .

Several authors<sup>8,9,12,27</sup> have suggested that the attenuation length follows the equation

$$\lambda = kE^p \quad (3)$$

for electrons with kinetic energy,  $E > 200$  eV, where  $p$  is a constant exponent. Errors associated with previous studies have been too large to allow a convincing determination of  $p$  in hydrocarbon films. Figure 3 plots  $\ln \lambda$  against  $\ln E$ . Clearly, three data points are insufficient to establish the functional form of eq 3. If we *assume* eq 3, we calculate a value of  $p = 1.0 \pm 0.1$ , where the error represents a greater than 95% confidence limit. We note that the systematic errors discussed above do not have a large effect on the value of  $p$ .

**Carbon (1s) peak of the Monolayer.** The intensities of the C(1s) peaks arising from the hydrocarbon chains of the monolayers of  $\text{HSC}_n\text{H}_{2n+1}$  on gold are shown in Figure 4. By analogy with eq 1 we can write down a model function<sup>28</sup> for the carbon intensity

$$C_n = C_\infty(1 - e^{-nd/\lambda \sin\theta}) \quad (4)$$

where  $C_\infty$  is the (unknown) intensity of the C(1s) peak from an infinitely thick monolayer.

Upon taking logarithms and rearranging to a form linear in  $n$ , eq 4 becomes

$$\ln(C_\infty - C_n) = \ln C_\infty - nd/\lambda \sin\theta \quad (5)$$

This equation can, in principle, be solved iteratively for the two unknown parameters  $C_\infty$  and  $\lambda$ . In practice, the C(1s) data do not fit this simple form. If one requires that  $C_0 = 0$ , a plot of  $\ln(C_\infty - C_n)$  against  $n$  is significantly curved, with a linear fit to the data yielding a value of  $\lambda = 43 \text{ \AA}$ ; if  $C_0$  is allowed to vary, one obtains an excellent linear fit with  $C_\infty = 490 \text{ Kcts}$  and  $\lambda = 32 \text{ \AA}$ , but with the physically unreasonable consequence that  $C_0 = -25 \text{ Kcts}$ . The deviations from eq 5 make it difficult to obtain a reliable value of  $\lambda$  from these data. One could obtain a better fit to the data by adding correction terms with suitable asymptotic behavior to the right hand side of eq 5, but such an exercise is futile unless the corrections are well-grounded in theory.

## Discussion

The plots of the XPS intensities of gold shown in Figure 2 show no statistically significant deviations from linearity, suggesting that eq 1 represents a good model for the scattering of the photoelectrons from the substrate. In addition, this linearity suggests that, to within experimental error, the number of adsorbed thiols per unit area of gold is independent of chain length since a change in number density with  $n$  would change either  $d$  or  $\lambda$  and hence cause curvature in the plots in Figure 2.

The values of  $\lambda$  derived from the data for gold (Table I) are in good agreement<sup>29</sup>

with those determined by Swalen<sup>9</sup> for multilayers of cadmium arachidate, suggesting that  $\lambda$  does not vary greatly with the thickness of the overlayer. The attenuation lengths also agree with inelastic mean free paths calculated from a simple model by Ashley<sup>30</sup> for polyethylene. Our attenuation lengths are significantly greater than those determined by Clark et al<sup>6</sup> for poly(p-xylylene) films, and lower than those obtained by Ringsdorf<sup>7</sup> for polymerized, Langmuir-Blodgett cadmium diacetylene multilayers, by King<sup>8</sup> for Langmuir-Blodgett barium stearate monolayers, or by Rei Vilar<sup>8</sup> for hexatriacontane films. None of these four systems is as well-defined as monolayers of thiols on gold.

Although the photoelectrons studied cover only a narrow energy range (940–1402 eV), many of the elements of interest to organic chemists -- C, O, N, P, Si, S, Cl, Br -- have their principal photoelectron peaks within this range when excited by Al K $\alpha$  radiation.<sup>31</sup> A combined IR/XPS study of monolayers of thiols on silver and copper would extend the energy range and confirm the accuracy of the values of  $\lambda$  determined from monolayers of thiols on gold.

The variation in  $\lambda$  with the kinetic energy of the photoelectrons differs from previous studies. The value of the exponent,  $p$ , in eq 3 of  $1.0 \pm 0.1$  is significantly larger than the 'universal' value of 0.5,<sup>12</sup> or the experimentally estimated values in the range 0.65 - 0.85.<sup>8,27</sup> Too much emphasis should not be placed, however, on the linearity of a fit derived from only three data points over a relatively narrow energy range.

The interpretation of the C(1s) data is less straightforward. The intensities of the photoelectron peaks do not follow the form of eq 4. The deviations from this simple relation cannot be explained by carbon contamination on the surface of the monolayer<sup>32</sup> or by the effects of elastic scattering.<sup>33</sup> A progressive increase with chain length in the number density of thiols adsorbed on gold could lead to behavior qualitatively similar to that observed. Infrared spectra<sup>14</sup> indicate that the packing of the monolayers with  $n < 10$  is different from the longer chains. The shorter thiols could plausibly have a lower surface

coverage than longer thiols ( $n > 10$ ), although no such effect is seen in the attenuation of the gold photoelectrons. For  $n > 10$ , neither infrared spectra<sup>14</sup> nor contact angle measurements<sup>10</sup> indicate gross changes in structure with chain length, in agreement with the data for gold. Although we feel that it is unlikely that structural changes in the monolayer are responsible for the unexpected form of the C(1s) intensities,<sup>34</sup> we cannot definitively rule out this possibility.<sup>35</sup> Further studies on other well-defined systems are necessary to determine whether the deviation in the C(1s) photoelectron intensities is an artifact of monolayers of thiols on gold, or is a general feature that needs to be included in detailed analyses of XPS data.

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<sup>2</sup> In this paper we will use the terms escape depth and attenuation length interchangeably to mean the thickness of material required to reduce the flux of the emitted photoelectrons by  $1/e$ , and denote both by  $\lambda$ .  $\lambda$  is not identical to the inelastic mean free path except in the absence of elastic scattering.

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- <sup>17</sup> The detailed structure of these shorter ( $n < 11$ ) monolayers is still under study.
- <sup>18</sup> These parameters result in a full width at half maximum of 1.4 eV for the Au(4f<sub>7/2</sub>) peak.

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<sup>20</sup> In a separate experiment values of  $Au_0$  (obtained by sputtering a gold film with an adsorbed layer of octadecanethiol with 3 keV  $Ar^+$  ions until the C(1s) signal disappeared) were within 5 % of the values predicted from the measured values of  $Au_{18}$  and the attenuation coefficients given in Table I, ignoring the effect of the sulfur atom of the thiol. In general, however, values of  $Au_0$  obtained by ion sputtering of a gold film are not directly comparable with values of  $Au_n$  due to changes in morphology induced by sputtering.

<sup>21</sup> Abrahamsson, S.; Larsson, G.; von Sydow, E. *Acta Crystallographica* 1960, 13, 770. A similar value is obtained if one simply assumes a tetrahedral bond angle and a typical C-C bond length of 1.54 Å.

<sup>22</sup> The chain tilt is conventionally measured from the surface normal, and the take-off angle from the surface parallel. The *direction* of the tilt in the chains probably varies over the size of the X-ray spot.

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<sup>28</sup> This equation is simply an exponential approximation to the discrete sum

$$C_n = \sum_{i=1}^n C_1 (1-d/\lambda \sin\theta)^{i-1}$$

where  $C_1$  is the intensity of the photoelectrons from a single monolayer of methylene groups. The sum has to be replaced by an exponential with care since errors are introduced into subsequent calculations. For example, if the value of  $\lambda$  calculated in the exponential approximation is used to predict the intensity expected from an infinitely thick hydrocarbon film ( $C_1 \lambda \sin\theta/d$ ) the estimate will be approximately 3% lower than the discrete sum of the carbon intensities. The exponential approximation does not change the linearity of the plots given by equations (1) and (5).

<sup>29</sup> The agreement with the values of  $\lambda$  obtained by Swalen on silver and gold is excellent (within 10 %). The value of  $\lambda$  obtained on indium is greater than the value predicted from our data. Indium, however, is the substrate for which the smallest number of data were accumulated, and for which the derived value of  $\lambda$  was least reliable.

<sup>30</sup> Ashley, J. C. *J. Electron Spectrosc.* 1982, 28, 177.

<sup>31</sup> The F(1s) peak does lie outside this energy range, but the values of  $\lambda$  determined here for hydrocarbons are probably not directly applicable to fluorocarbons anyway.

<sup>32</sup> Comparable low-energy fluorinated surfaces (e.g. a monolayer of  $\text{HS}(\text{CH}_2)_2(\text{CF}_2)_5\text{CF}_3$  on gold) show less than a monolayer (in terms of  $\text{CH}_2$  groups) of adventitious carbon by XPS. Carbon contamination would, in any event, lead to a positive value of  $C_0$ .

<sup>33</sup> The data obtained for gold, together with previous Monte Carlo simulations,<sup>22</sup> suggest that elastic scattering by the hydrocarbon monolayer is not important. High-angle elastic scattering from the gold would increase the intensity of the  $\text{C}(1s)$  peak at low chain lengths, contrary to what is observed. If (e.g. for geometrical reasons) inelastic scattering by the methyl group was less than by the methylene groups, an exponential curve with an apparent negative intercept would be observed. The effect of such differential scattering, however, would be too small to explain the data satisfactorily.

<sup>34</sup> The ellipsometric thickness (Ref. 10) of monolayers of *n*-alkanethiols on gold is also linear with chain length. The slope of a plot of ellipsometric thickness against chain length is  $1.5 \text{ \AA}$  per  $\text{CH}_2$ . We do not use this value for  $d$  since a slope of  $1.5 \text{ \AA}/\text{CH}_2$  is greater than that theoretically possible, even for chains oriented normal to the surface. This discrepancy probably arises from inadequacies in our model for analyzing the ellipsometric constants.

<sup>35</sup> It is not simple to derive reliable escape depths from the  $\text{C}(1s)$  data, which begs the question: How accurate are compositions of thin films that are calculated using escape depths derived from attenuation of substrate signals? To approach this question, the intensities of the  $\text{C}(1s)$  photoelectrons were estimated using  $\lambda$  calculated from the data for gold, and a value of  $C_\infty = 490 \text{ Kcts}$ , derived from an exponential fit to the observed  $\text{C}(1s)$  intensities. The differences between the observed and estimated photoelectron intensities were less than 10 % of the carbon intensity for all values of  $n$ : errors at least as large as

this are likely to arise from other sources in most experiments.

**Table I.** Attenuation Lengths Calculated from XPS Intensities of the Photoelectrons of the Gold Substrate

Photoelectron	K.E.(eV)	slope	$\lambda(\text{\AA})^a$
Au(4f <sub>7/2</sub> )	1402	-0.046	42 $\pm$ 1.4
Au(4d <sub>5/2</sub> )	1151	-0.056	34 $\pm$ 1.5
Au(4p <sub>3/2</sub> )	940	-0.068	28 $\pm$ 0.8

<sup>a</sup> The errors in  $\lambda$  represent 95% confidence levels based on the random errors in the data in Fig. 2.

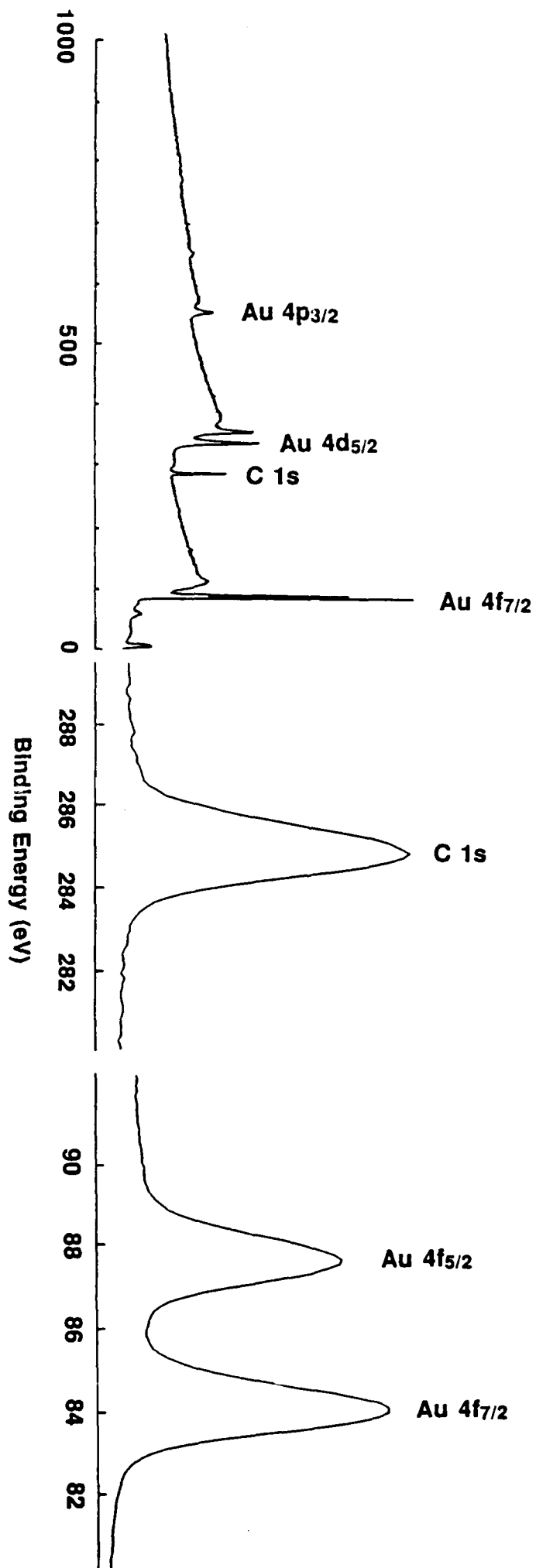
### Figure Captions

**Figure 1.** X-ray photoelectron spectra of a monolayer of octadecanethiol on gold. The survey spectrum (left) shows the core-levels used to calculate the attenuation lengths. High resolution spectra (right) of the C(1s) and Au(4f<sub>7/2</sub>) regions are shown to indicate the signal-to-noise ratio in these studies.

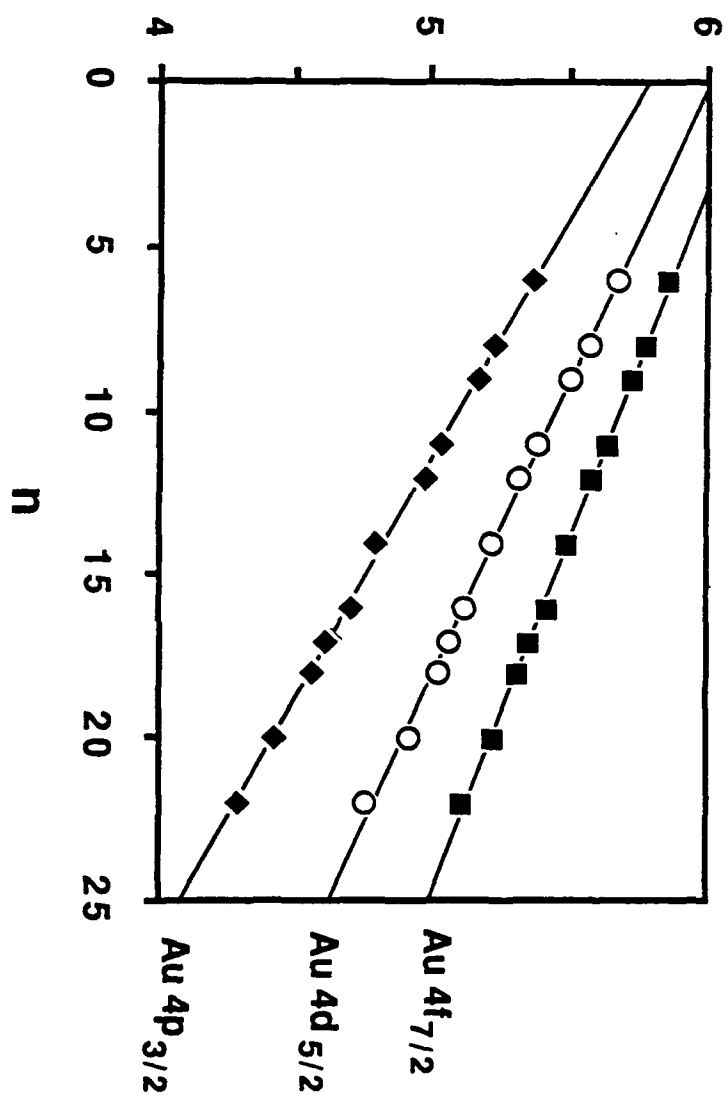
**Figure 2.** Intensities of the X-ray photoelectrons from the gold substrate as a function of the number of carbons,  $n$ , in the thiol for monolayers of  $\text{HSC}_n\text{H}_{2n+1}$  assembled on gold. The data for Au(4f<sub>7/2</sub>) have been offset vertically for clarity; the absolute value of the ordinate is a function of instrumental parameters, only the slope is important here.

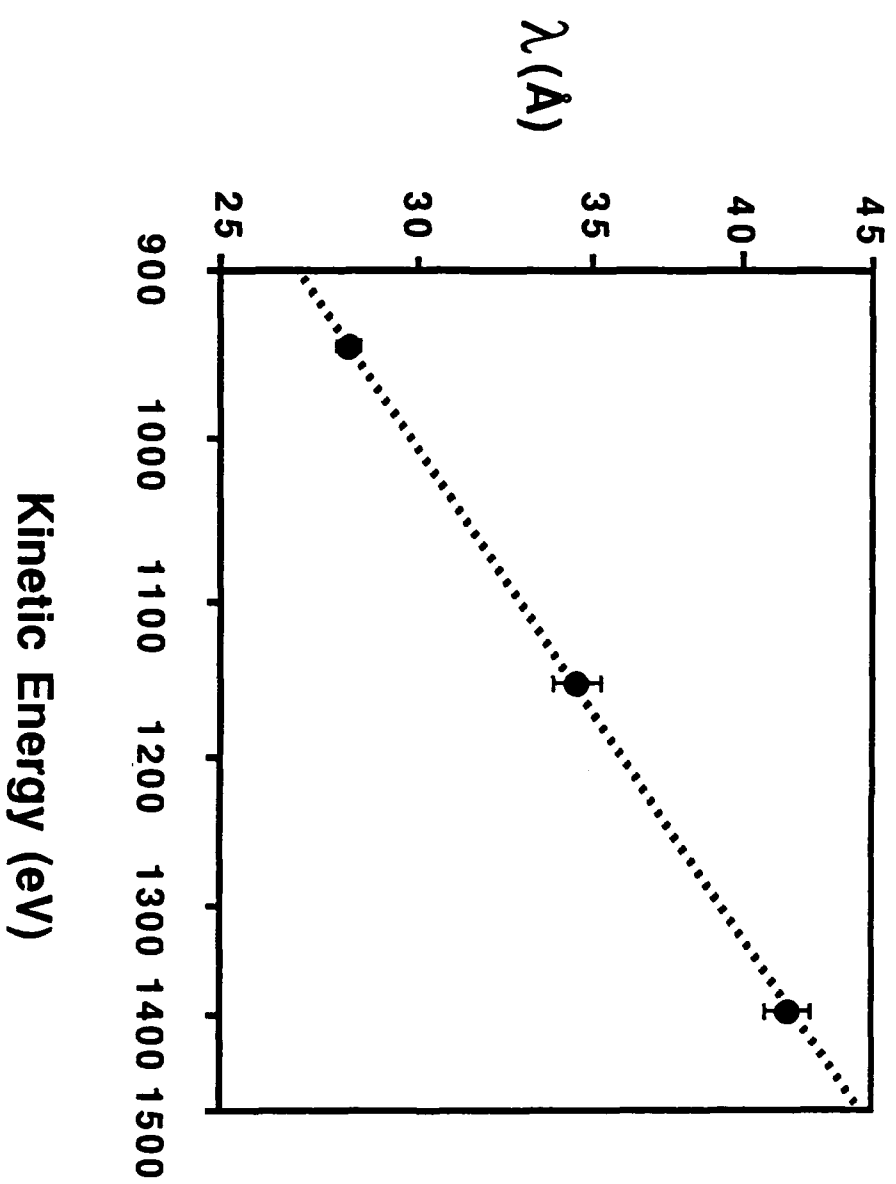
**Figure 3.** Double log plot of attenuation length for photoelectrons of varying kinetic energy. The error bars are 95% confidence limits in the random error.

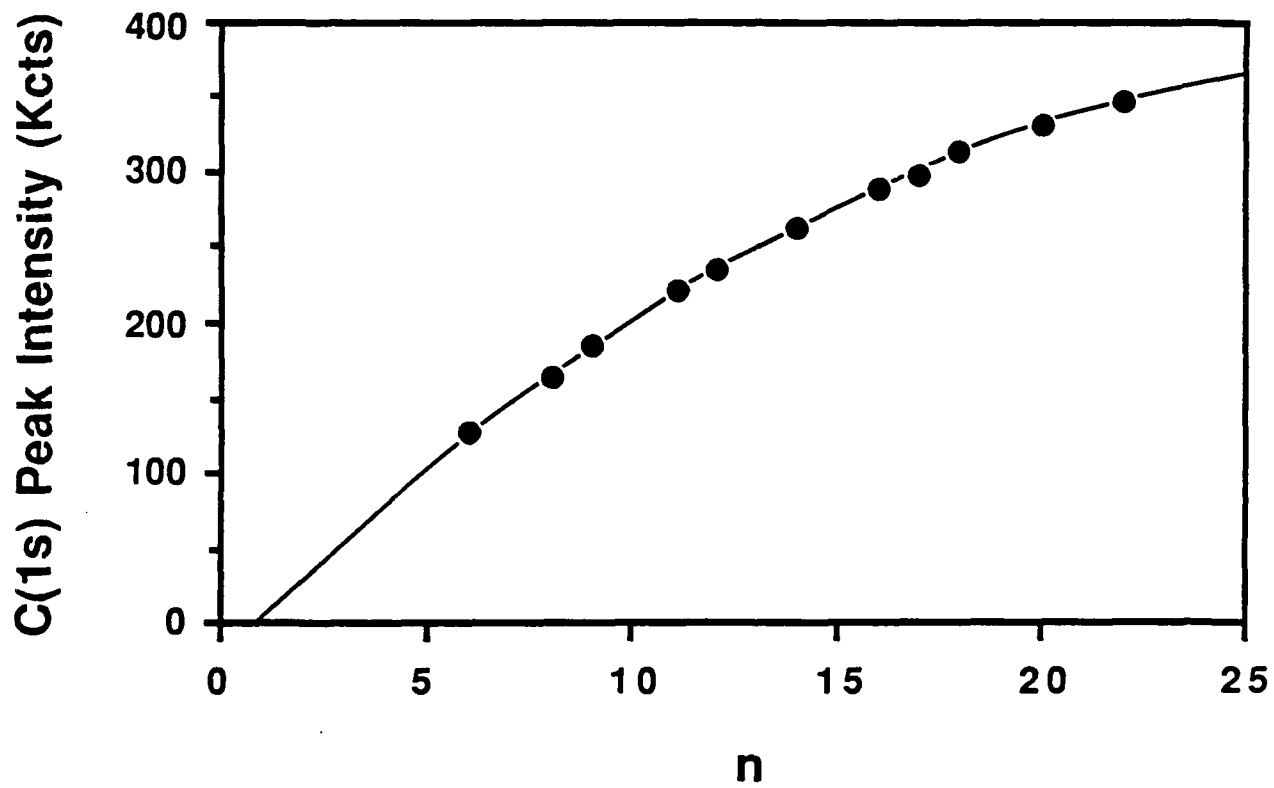
**Figure 4.** Intensities of the C(1s) photoelectrons arising from monolayers of  $\text{HSC}_n\text{H}_{2n+1}$  assembled on gold, as a function of the chain length,  $n$ . The solid line is a cubic fit to the data ( $\text{C}(1s) = -23 + 28.9n - 0.70n^2 + 0.007n^3$  Kcts).



ln (XPS Intensity)







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